歐文日本化學會誌　第一卷第九號

大正十五年九月二十五日印刷
大正十五年九月二十八日發行

編輯兼發行者　東京帝國大學理學部內　松原行一
印刷者　東京市日本橋區兜町二番地　神谷岩次郎
發行所　東京帝國大學理學部內　日本化學會事務所
印刷所　東京市日本橋區兜町二番地　東京印刷株式會社
賣捌所　東京市日本橋區通三丁目十四番地　丸善株式會社

# DETERMINATION OF HIGH TEMPERATURE BY THE EFFUSION AND THE TRANSPIRATION OF GAS.

By Yohei YAMAGUCHI.

Received August 28, 1926. Published October 28, 1926.

The rates of flow of gases at high temperatures were studied by Emich[1] for the determination of gas densities. I have undertaken some experiments to test whether such a phenomenon can be utilized for the determination of high temperature or not.

**1. The Relation between the Temperature and the Rate of Effusion.** The apparatus used for the measurement of the rate of effusion is shown in Fig. 1. On the stem of a glass vessel resembling Ostwald's viscosimeter, two marks A and B were etched, the volume between them being about 100 c.c. After the bulb was filled with a certain quantity of petroleum of high boiling point (215–225°), the lower part of the vessel is immersed in a thermostat at 25°. T is a quartz tube having a small opening at its end through which the gas effuses and is placed in an electric furnace. When the temperature of the tube became constant, the stop-cock C is opened and a certain quantity of dry air is blown into the system by means of D in order to push

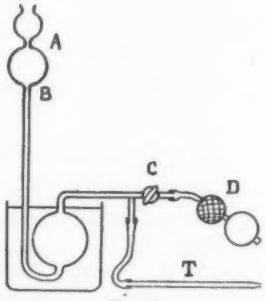



Fig. 1

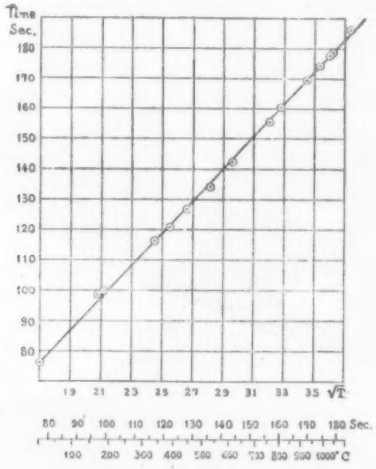



Fig. 2

(1) Emich, *Monatsh.*, **24** (1903), 747; **26** (1905), 505.

up the petroleum above the mark A. Hereupon the stop-cock is closed and the time in which the petroleum falls down from A to B is measured. The relation between the measured time and the temperature is shown in Table 1[1].

TABLE 1.

| Time in sec. ($t$) | Temp. C°. | Abs. temp. ($T$) | log $T$ | $\sqrt{T}$ | $t_{calc.}$ |
|---|---|---|---|---|---|
| 76.4 | 17 | 290 | 2.4624 | 17.03 | 75.4 |
| *115.8 | 328 | 601 | 2.7789 | 24.52 | (115.8) |
| 126.6 | 434 | 707 | 2.8494 | 26.59 | 127.0 |
| 142.9 | 605 | 878 | 2.9435 | 29.63 | 143.4 |
| *170.0 | 922 | 1195 | 3.0774 | 34.57 | (170.0) |
| 177.9 | 1033 | 1306 | 3.1158 | 36.13 | 178.4 |
| 185.5 | 1125 | 1398 | 3.1456 | 37.40 | 185.3 |

Fig. 2 shows that there is a linear relation between the time ($t$) and the square root of the absolute temperature ($T$). Thus we can put,

$$t=a+b\sqrt{T} \quad \cdots\cdots(1)$$

Taking out two pairs of observed values and calculating the constants $a$ and $b$, we obtain, $t=5.393\sqrt{T}-16.44$. The times of effusion are calculated by this equation from the observed temperatures and are shown in the last column of Table 1. The calculated times are in good agreement with the observed ones.

*Theoretical.* The definite quantity of gas corresponding to the volume between the marks A and B, will expand to a larger volume at the opening of the quartz tube where the temperature is high. Hence if the velocity of effusion be independent of temperature, the time of effusion ($t$) is proportional to the absolute temperature ($T$),

$$t \propto \text{volume} \propto T \quad \cdots\cdots(2)$$

Now the time of flow of gases by effusion under a given pressure difference is also inversely proportional to the mean velocity ($v$) of the gas molecules, and the mean velocity is, as is well known, proportional to the square root of the absolute temperature,

$$t \propto \frac{1}{v} \propto \frac{1}{\sqrt{T}} \quad \cdots\cdots(3)$$

Combining (2) and (3), we have,

(1) More detailed data were published in the *Journal of the Chemical Society of Japan*, **43** (1922), 1.

$$t \propto \sqrt{T}, \qquad \text{or} \qquad t = b\sqrt{T} \quad \cdots\cdots\cdots\cdots (4)$$

where $b$ is a constant. The constant $a$ in the empirical equation (1) may be considered to be a correction term to the equation (4) obtained by such a simple deduction.

**2. The Relation between the Temperature and the Rate of Transpiration.** High temperatures can also be determined by measuring the rate of transpiration of gases through a capillary tube of quartz. The apparatus employed for the purpose is similar to that used above, excepting that the quartz tube for effusion is now replaced by another quartz tube of about 3 mm. diameter, one end of which is elongated so as to form a capillary. Some of the data obtained from the experiments are shown in Table 2.

TABLE 2.

| Time in sec. ($t$) | log $t$ | Temp. C°. | Abs. temp. ($T$) | log $T$ | $T_{calc.}$ |
|---|---|---|---|---|---|
| 61.0 | 1.7853 | 20.5 | 293.5 | 2.4676 | 288 |
| 79.4 | 1.8998 | 125.5 | 398.5 | 2.6004 | 395 |
| * 94.2 | 1.9741 | 200.2 | 473.2 | 2.6751 | 478 |
| 116.7 | 2.0671 | 333 | 606 | 2.7822 | 599 |
| *151 | 2.1790 | 487 | 760 | 2.8808 | 767 |
| 212 | 2.3263 | 739 | 1012 | 3.0051 | 1025 |
| *241 | 2.3820 | 848 | 1121 | 3.0496 | 1132 |
| 264.2 | 2.4219 | 929 | 1202 | 3.0799 | 1211 |
| 300 | 2.4771 | 1046 | 1319 | 3.1202 | 1321 |

The value of log $T$ can well be represented by an equation of the second order of log $t$, thus

$$\log T = a + b \log t + c (\log t)^2 \cdots\cdots\cdots\cdots (5)$$

Evaluating the constants $a$, $b$ and $c$ from three data marked with asterisks in Table 2, we get the following empirical equation,

$$\log T = -1.0967 + 2.7376 \log t - 0.4178 (\log t)^2 \cdots\cdots (6)$$

The values of $T_{calc.}$ in Table 2, which were obtained from this equation, are in good agreement with the observed values.

**3. The Relation between the Temperature and the Pressure of Gas Transpirating at a Definite Rate.** The temperature of transpirating gas can also be determined by measuring the pressure necessary to keep a constant rate of flow of the gas. The apparatus shown in Fig. 3 was used for the purpose. If water is allowed to run into the bottle A from the tube B, the air in

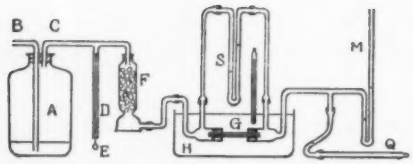



Fig. 3

A, being replaced by the water, will be expelled from the tube C under a certain pressure. The quantity of the air flowed out through the tube C could be controlled by regulating the water supply and by moving a copper wire E inserted in a capillary tube D. F is a drying tower filled with $CaCl_2$. G is a capillary flowmeter immersed in a thermostat H of 25°. S and M are manometers for measuring the pressure difference. Q is a quartz tube of about 3 mm. diameter, one end of which is elongated so as to form a capillary. If a temperature elevation takes place at the capillary part of Q, then the velocity of the air stream which passes through the capillary will decrease. Consequently the pressure of the supplied air must be increased, in order to keep the quantity of the air allowed to pass through the capillary at a constant value. This increase of the pressure is read by the manometer M. Thus in carrying out the experiment, the temperature at the capillary part of the quartz tube Q and the pressure difference indicated by the manometer M should be read off, under the constant pressure difference of the manometer S. Potroleum of high boiling point was used for the manometer S and water for the manometer M. Two series of experiments have been performed, when the pressure difference indicated by the manometer S are 10 cm. and 20 cm. in petroleum column respectively. The adridged data are shown in Table 3. Taking $\log p$ and $\log T$ as coordinates, there is found a linear relation between them, as is shown in Fig. 4.

TABLE 3.

| Press. diff. of flowmeter S, in cm. of petroleum. | Press. of air in cm. of water indicated by manometer M. ($p$) | $\log p$ | Abs. temp. ($T$) | $\log T$ | $p_{calc.}$ | $T_{calc.}$ |
|---|---|---|---|---|---|---|
| 10 | 1.38 | 0.1399 | 290 | 2.4624 | 1.39 | 288 |
| | 2.52 | 0.4014 | 437 | 2.6405 | 2.52 | 437 |
| | 4.73 | 0.6749 | 675 | 2.8293 | 4.72 | 676 |
| | 7.37 | 0.8675 | 915 | 2.9614 | 7.33 | 918 |
| | 10.28 | 1.0120 | 1153 | 3.0618 | 10.24 | 1156 |
| | 14.42 | 1.1590 | 1478 | 3.1697 | 14.67 | 1461 |
| 20 | 3.92 | 0.5933 | 287 | 2.4579 | 3.96 | 285 |
| | 6.98 | 0.8439 | 439 | 2.6425 | 7.05 | 436 |
| | 10.12 | 1.0051 | 573 | 2.7582 | 10.12 | 573 |
| | 16.44 | 1.2159 | 828 | 2.9178 | 16.66 | 819 |
| | 26.28 | 1.4196 | 1160 | 3.0645 | 26.37 | 1157 |
| | 36.00 | 1.5563 | 1479 | 3.1700 | 36.67 | 1459 |

*Theoretical.* In order to keep the quantity of the gas passing in a given interval through the quartz capillary always constant, notwithstanding the temperature of the capillary is elevated, the pressure of the gas must be increased. If we assume that all other conditions are constant, the gas must be compressed to its initial volume in order that the quantity of the transpirated gas should be kept invariably, and the pressure must change proportional to the absolute temperature, $p \infty T$. When the temperature is elevated, however, there takes place in the gas not only the increase of volume but also the increase of viscosity, so that the pressure must be increased a little more on account of the increase of viscosity. Let $\eta$ be the viscosity, then we have

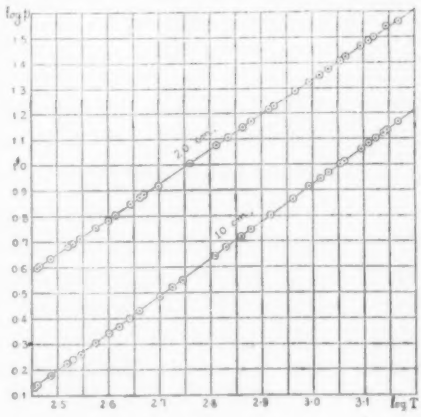



Fig. 4

$$p \infty \eta, \quad \cdots\cdots(8)$$

therefore $p \infty \eta T,$

or $$\frac{p}{p_0} = \frac{\eta T}{\eta_0 T_0} \quad \cdots\cdots(9)$$

According to Sutherland the relation between the viscosity and the absolute temperature $T$ may be expressed by the following equation.

$$\frac{\eta}{\eta_0} = \left(\frac{T}{T_0}\right)^{\frac{1}{2}} \frac{1+\frac{c}{T_0}}{1+\frac{c}{T}} \quad \cdots\cdots(10)$$

so $$p = p_0 \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \frac{1+\frac{c}{T_0}}{1+\frac{c}{T}} \quad \cdots\cdots(11)$$

or $$p = k T^{\frac{3}{2}} \left(1+\frac{c}{T}\right)^{-1} \quad \cdots\cdots(12)$$

If $c$ is small, and $T$ is large in equation (12), we may put

$$\log p = \log k + \tfrac{3}{2} \log T \quad \cdots\cdots(13)$$

This shows that the relation between $\log p$ and $\log T$ is linear, agreeing with the results shown in Fig. 4. Assuming a more general form,

$$\log p = a \log T + b \quad \cdots\cdots (14)$$

two constants $a$ and $b$ being calculated by the method of least square from the observed data, thus :

Press. diff. on manometer S = 10 cm., $a = 1.4462$, $b = -3.4176$.

Press. diff. on manometer S = 20 cm., $a = 1.3582$, $b = -2.7414$.

In equation (13) which is derived from Sutherland's formula, the constant $a$ is $\frac{3}{2}$. According to the above results, the value of $a$ is smaller than $\frac{3}{2}$, but not very different from it. The values of the pressure $p$ calculated by applying the above values of $a$ and $b$ in equation (14) are shown in the sixth column of Table 3. The calculated values are in good agreement with the observed values.

For the determination of temperature by measuring the pressure of gases, equation (14) must be transformed into the following form.

$$\log T = a' \log p + b' \quad \cdots\cdots (15)$$

The values of $a'$ and $b'$ are found as follows.

Press. diff. on manometer S = 10 cm., $a' = 0.69146$, $b' = 2.3632$.

Press. diff. on manometer S = 20 cm., $a' = 0.73623$, $b' = 2.0183$.

The values of the temperature ($T_{\text{calc.}}$), corresponding to the observed $p$, calculated from equation (15) are shown in the seventh column of Table 3. Comparing the calculated values with observed values of $T$, we see that this method may be used for the determination of high temperatures with equally good result as other pyrometers.

It was thus shown that this method is applicable from common temperature up to about 1200°C. For lower temperatures experiments have not yet been undertaken. Assuming that the equation (12) could be applied also in this case, the linear equation (13) hardly be employed, as the factor $1 + c/T$ becomes greater. The curve representing the required relation should deviate from the straight line which represents equation (13), as the temperature falls. As to the method of experiment, the apparatus shown in Fig. 3 can be employed without any alterlation for lower temperatures. At much lower temperatures, however, the pressure difference in the manometer M will be so small that the readings becomes very difficult. For this reason it will be better to modify the method of measurement, namely, to exchange the rôle of two manometers, and the difference in S should be read off, the difference in M being maintained to be constant, as the difference in S becomes greater according as the temperature falls.

**Summary.**

Three methods have been studied for the purpose of determining high temperature by the observation of the rate of flow of gas. In the first method the temperature is determined by the effusion of gas, time necessary for the escape of a definite quantity of gas being observed. The following equation can be applied for the range from the common temperature up to about 1000°,

$$t = a + b\sqrt{T},$$

where $T$ is the temperature, $t$ is the time of effusion of air which passes through a quartz opening, and $a$ and $b$ are constants. This method might be useful, as the apparatus employed for this purpose is very simple and the relation between time and temperature can be represented by a simple equation.

In the second method, the temperature is measured by the transpiration of gases through a quartz capillary, the time of flow being measured also in this case. In the range from common temperature up to about 1000°, the logarithms of the absolute temperature can be expressed as an equation of second order of the logarithms of the time.

In the third method, the increase of the pressure necessary to maintain a constant rate of flow was observed. In the range from the common temperature up to about 1200°, there was found a linear relation between the logarithm of pressure and that of absolute temperature.

In conclusion I express my best thanks to Prof. K. Ikeda for his kind guidance.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

---

# THE RADIOACTIVITY OF THE RUBIDIUM EXTRACTED FROM THE LEPIDOLITE AND ZINNWALDITE OF JAPAN.

By **Satoyasu IIMORI** and **Jun YOSHIMURA.**

Received September 11, 1926. Published October 28, 1926.

Nothing is known about the radioactive serial genesis of potassium and rubidium, and there remain several important subjects still for decision. It has often been considered that the feebleness of their radioactivity might be ascribed to their inferior isotopes admixed, viz. $K^{41}$ and $Rb^{87}$. Accord-

ing to this supposition the activity of these elements might not be always the same when the mineral source of the elements are different. A number of preparations of potassium salt of different origins were ever examined for the activity, and it was pointed out that a fixed result was consistently obtained[1]; but on rubidium no study of this line has yet been made. In the present work, it was undertaken, therefore, to prepare the pure rubidium preparations from some Japanese lithia micas and to compare their activities with that of the Kahlbaum's preparation which is probably derived from the Stassfurt deposits.

**Method of Separating the Rare Alkalies.** The separation of the rare alkalies was effected by adopting a special procedure improved by the authors. The method was based upon the sparing solubility of caesium antimony chloride[2] and rubidium stannic chloride[3] in concentrated hydrochloric acid. On treating the dried solid mixture of alkali chlorides with concentrated hydrochloric acid (sp. gr., 1.185), the most part of sodium chloride, which is least soluble in hydrochloric acid, is first removed, and subsequently caesium and rubidium are precipitated in presence of potassium and lithium from the filtrate, one after another by adding suitable quantities of hydrochloric acid solutions of antimony chloride and stannic chloride respectively. After removal of the tin and antimony as sulphides, the final filtrate is evaporated up to dryness, and the residue which contains the chlorides of whole lithium and potassium as well as a trifling remainder of sodium, is now put together with the first residue of sodium chloride and used for the estimation of lithium, sodium and potassium which are quite readily separable by the usual method. In carrying out this process, the volume of solutions, in which the precipitations occur, is very important and notably influences every precipitations, especially that of caesium antimony chloride. The solubilities of all the alkali chlorides and double chlorides in concentrated hydrochloric acid (1.185), which are given in Table 1 and Table 2,

TABLE 1.

| Approx. Solubility of Alkali Chlorides in Hydrochloric Acid (sp. gr., 1·185) at 16~17°C. | | |
|---|---|---|
| Chlorides. | Gr. chloride which are dissolved in 100 c.c. HCl. | C.c. HCl, in which 1gr. chloride dissolves |
| CsCl | 55.3 | 1.8 |
| RbCl | 16.1 | 6.2 |
| LiCl | 31.3 | 3.2 |
| KCl | 1.1 | 90.0 |
| NaCl | 0.1 | 1000.0 |

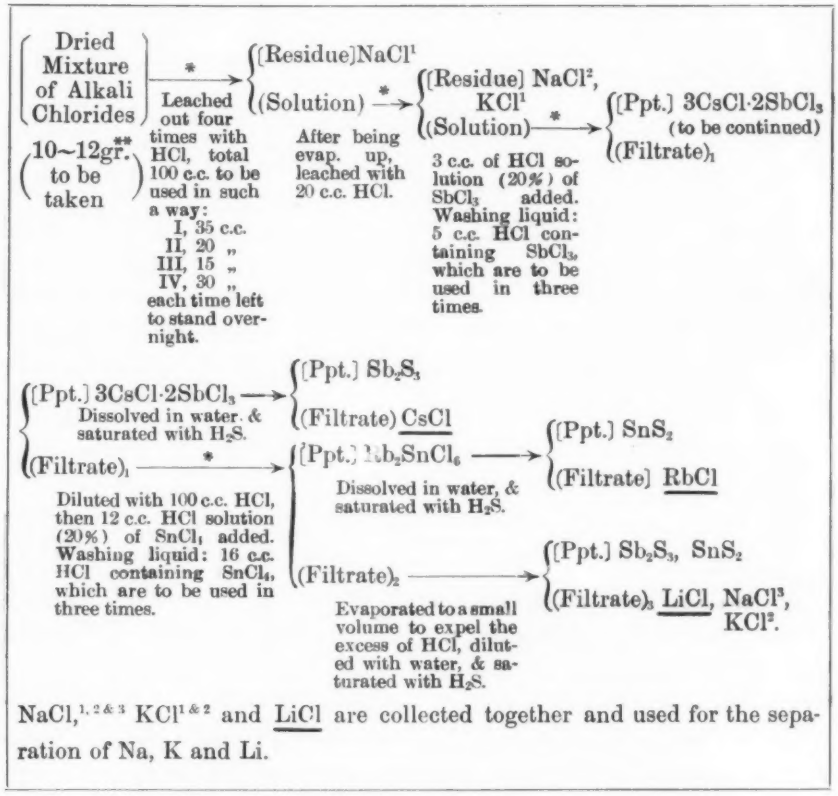
TABLE 2.

| Solubility of Double Chlorides in HCl (sp. gr., 1·185) at 20°C. | |
|---|---|
| "Double" chlorides | Gr. double chloride which exists dissolved in 100 c.c. HCl solution. |
| $3CsCl{\cdot}2SbCl_3$ | 0.4599 (=0.2416 CsCl or 0.2021 $Cs_2O$) |
| $Rb_2SnCl_6$ | 0.0194 (=0.0093 RbCl or 0.0072 $Rb_2O$) |
| $K_2SnCl_6$ | 0.1892 (=0.0689 KCl or 0.0435 $K_2O$) |

(1) N. R. Campbell, *Proc. Cambridge Phil. Soc.*, **14** (1908), 15.
W. Biltz & E. Marcus, *Z. anorg. Chem.*, **81** (1913), 369.
(2) R. Godeffroy, *Ber.*, **7** (1874), 376; *Liebig's Ann. Chem.*, **181** (1876), 176.
(3) S. P. Sharples, *Am. J. Sci.*, (2), **97** (1869), 178.

as well as the mutual effects upon solubilities were therefore determined, and a scheme of procedure was established. Table 3 illustrates the outline of the scheme. The vessels to be employed for the separation must strictly be

TABLE 3.


Dried Mixture of Alkali Chlorides
10~12gr.** to be taken
*
Leached out four times with HCl, total 100 c.c. to be used in such a way:
I, 35 c.c.
II, 20 „
III, 15 „
IV, 30 „
each time left to stand over-night.
(Residue)NaCl¹
(Solution)
After being evap. up, leached with 20 c.c. HCl.
*
(Residue) NaCl², KCl¹
(Solution)
3 c.c. of HCl solution (20%) of SbCl₃ added. Washing liquid: 5 c.c. HCl containing SbCl₃, which are to be used in three times.
*
(Ppt.) 3CsCl·2SbCl₃ (to be continued)
(Filtrate)₁
(Ppt.) 3CsCl·2SbCl₃
Dissolved in water. & saturated with H₂S.
(Ppt.) Sb₂S₃
(Filtrate) CsCl
(Filtrate)₁
*
Diluted with 100 c.c. HCl, then 12 c.c. HCl solution (20%) of SnCl₄ added. Washing liquid: 16 c.c. HCl containing SnCl₄, which are to be used in three times.
(Ppt.) Rb₂SnCl₆
Dissolved in water, & saturated with H₂S.
(Ppt.) SnS₂
(Filtrate) RbCl
(Filtrate)₂
Evaporated to a small volume to expel the excess of HCl, diluted with water, & saturated with H₂S.
(Ppt.) Sb₂S₃, SnS₂
(Filtrate)₃ LiCl, NaCl³, KCl².

NaCl,[1,2&3] KCl[1&2] and LiCl are collected together and used for the separation of Na, K and Li.

* Asbestos filter is to be employed for the filtration.

** Limiting amounts (gr.) of chlorides to be taken for separation:—
CsCl: 0·5, RbCl: 1·5, NaCl: 2·0, LiCl: 5·0 and KCl: 5·0, viz. total: 14·0 gr.

avoided from moisture, consequently the asbestos filters, extracting flasks, etc. were used to kept in a large desicator. The process proved to give a quite satisfactory result.

**The Rubidium Content of the Lithia Micas of Japan.** Since the rubidium usually occurs associated with lithium, all available specimens of

Japanese lithia and lithia iron micas were preliminary analyzed for alkalies by the ordinary method of J. Lawrence Smith with the result shown in Table 4.

TABLE 4.

| Micas analyzed | | $Li_2O$(%) | $Na_2O$(%) | $K_2O$(%) |
|---|---|---|---|---|
| Tanokami zinnwaldite | {large crystals, transparent with purple shade.} | 4.24 | 5.00 | 7.89 |
| 〃 〃 | {largec rystals, transparent with brown shade.} | 3.63 | 2.18 | 7.52 |
| Naegi zinnwaldite | {large crystals, transparent with brown shade.} | 2.31 | 5.82 | 8.35 |
| Nagatori lepidolite | {congregated mass of quartz and scaly mica.} | 2.49 | 3.20 | 9.13 |
| 〃 〃 | { 〃 〃 , a diff. lump. } | 1.94 | 2.70 | 6.71 |

For the extraction of rubidium the Tanokami zinnwaldite and Nagatori lepidolite were dealt with, and the separation was carried out according to the above mentioned method. The results obtained were as follows:

TABLE 5.

| Micas | Amount taken (gr.) | $Rb_2SO_4$ yielded (gr.) | $Rb_2O$ % |
|---|---|---|---|
| Tanokami zinnwaldite (1st sample): | 60.11 | 0.6916 | 0.81 |
| 〃 〃 (2nd sample): | 60.43 | 0.8538 | 0.98 |
| Nagatori lepidolite : | 60.05 | 0.8214 | 0.96 |

It has been proved spectrographically that all of these sulphate preparations contained no impurity but very small amount of caesium which could not be thrown down by antimony chloride in the course of separation. This amount of caesium contained in the preparations was so ascertained from the scale of procedure that it never exceeds 0.08% at most referred to to the sample.

**The Radioactivity of the Rubidium Sulphate Preparations.** The $\beta$-ray activity of these preparations was measured by means of a sensitive alpha-ray electroscope and compared with that of the Kahlbaum's preparation. The results obtained are set out in Table 6.

TABLE 6.

| Sample | Thickness of layer (gr./cm.$^2$) | Activity (div./hr.) | Comparison of activity |
|---|---|---|---|
| The $\beta$-ray standard ($U_3O_8$) | — | 1425* | 100 |
| Rubidium sulphate preparation of Kahlbaum | 0.0294 | 3.5 per gr. | 0.246 |
| Rubidium sulphate prep. from Tanokami zinnwaldite | 0.0116 | 3.4 „ | 0.239 |
| Rubidium sulphate prep. from Nagatori lepidolite | 0.0256 | 3.6 „ | 0.253 |

* This is the limiting activity of the $\beta$-ray from the uranium oxide employed as the standard, corrected for the absorption by the aluminium foil of 0.05 mm. thickness used to cover the standard.

It will be seen that no marked difference in the activity of these preparations could be detected, the activities expressed per gr. in those layer thicknesses indicated in the above table having been directly compared with the limiting $\beta$-ray activity of the uranium oxide as the absorption coefficient of the prepatation for the $\beta$-ray from rubidium is unknown. Thus, it may be concluded that the activity of rubidium so far studied in the present work does not depend upon the mineral, from which the element has been extracted.

The Institute of Physical and Chemical Rearch,
Hongo, Tokyo.

---

# ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. IV. THE ACTION ON CYCLOHEXANOL AND ITS DERIVATIVES.

By Harushige INOUE.

Received July 15, 1926. Published October 28, 1926.

Chavanne and Roelan[1] have observed that cyclohexanol, by the contact action of alumina, was decomposed at 160° into cyclohexene and water, and the same chemical reaction of the alcohol was also noticed by Bouveault[2] when clay was used as a catalyst at 300°. Japanese acid earth behaves as a catalyst, as mentioned in the previous articles of this subject,[3] in a some-

(1) Chavanne and Roelan, *Chem. Zentr.*, **80** (1909) I, 73.
(2) Bouveault, *Bull. Soc. Chim.*, [4] **3** (1908), 118.
(3) Inoue, this journal, **1** (1926), 157, 177 & 197.

what different way from alumina, clay or silica which were regarded as the principal constituents of the Japanese acid earth, and the present research was undertaken in the expectation of getting some different results, in some respects, from those mentioned by Chavanne and Roelan, and also by Bouveault.

The cyclohexanol used in the experiment, was prepared from pure phenol by catalytic reduction with reduced nickel and pure hydrogen under 20 atmospheric pressures at 180°, which shows: b.p. 135° under 84.6 mm.; m.p. below 18°; $d_{20}^{20}=0.9547$; $n_D^{20}=1.4650$.

Cyclohexanol[1] was passed with air, or $CO_2$ on the catalyst heated at 200° and 330° respectively, and the reaction product, which consisted of oily and water layers, was fractionated after being dried with anhydrous sodium sulphate as usual, and each fraction was determined its density and the index of refraction and the results are shown in Tables 1–4.

TABLE 1.

50.9 gr. of cyclohexanol yielded 23.4 gr. oil ($d^{20}=0.8143$) at 200°, in an atmosphere of air.

| Fraction | Yield gr. | $d_{20}^{20}$ | $n_D^{20}$ |
|---|---|---|---|
| 80–82° | 12.2 | 0.7971 | 1.44476 |
| 82–84°.5 | 4.7 | 0.8007 | 1.44070 |
| 85–90° | 1.7 | 0.8045 | — |
| above 90° | 3.3 | 0.8942 | 1.48078 |

TABLE 2.

52 gr. of cyclohexanol yielded 26 gr. oil ($d^{20}=0.8362$) at 200°, in an atmosphere of $CO_2$.

| Fraction | Yield gr. | $d_{20}^{20}$ | $n_D^{20}$ |
|---|---|---|---|
| 80–82° | 6.6 | 0.7941 | 1.43622 |
| 82–84°.5 | 10.3 | 0.7962 | 1.43772 |
| 85–90° | 0.7 | 0.8059 | 1.44165 |
| 90–225° | 1.4 | 0.8774 | 1.47215 |
| Residue | 3.3 | 0.9044 | 1.48881 |

(1) Inoue, *J. Soc. Chem. Ind. Japan*, 27 (1924), 553.

TABLE 3.

51.4 gr. of cyclohexanol yielded 32.6 gr. oil ($d^{20}=0.8123$) at 330°, in an atmosphere of air.

| Fraction | Yield gr. | $d_{20}^{20}$ | $n_D^{20}$ |
|---|---|---|---|
| 71–73° | 3.2 | 0.7512 | 1.41177 |
| 73–75° | 8.1 | 0.7536 | 1.41321 |
| 75–80° | 3.3 | 0.7563 | 1.41510 |
| 80–93° | 1.6 | 0.7741 | 1.42140 |
| 93–215° | 3.9 | 0.8896 | 1.55273 |
| Residue | 6.6 | 0.9644 | 1.56521 |

TABLE 4.

49.7 gr. of cyclohexanol yielded 32.8 gr. oil ($d^{20}=0.8065$) at 330°, in an atmosphere of $CO_2$.

| Fraction | Yield gr. | $d_{20}^{20}$ | $n_D^{20}$ |
|---|---|---|---|
| 71–73° | 2.2 | 0.7492 | 1.41282 |
| 73–75° | 11.5 | 0.7518 | 1.41326 |
| 75–80° | 3.6 | 0.7558 | 1.41510 |
| 80–93° | 1.5 | 0.7678 | 1.42370 |
| 93–215° | 3.7 | 0.8975 | 1.50522 |
| Residue | 6.4 | 0.9646 | 1.55198 |

As will be seen in Tables 1 and 2 the fractions with b.p. 80–82°, and b.p. 82–84°.5 which are main parts of the reaction product obtained at 200°, as indicated by the physical constants, seem to composed of the cyclohexene resulting by the dehydration of cyclohexanol, which was confirmed by isolating adipic acid (m.p. 153–154°), from the oxidation product of the fractions with nitric acid following the directions denoted by Markonikoff.[1]

While the reaction product resulting at 330°, consisted principally of the fraction with b.p. 73–75° which agrees in density and index of refraction with methyl-cyclopentane isolated by Markonikoff[2] from the low-boiling fractions of Caucasian petroleum, and also by Young[3] from American oil. For the confirmation of the fraction, it was subjected to the oxidation with nitric acid according to the directions of Aschan,[4] and acetic and succinic acids with a

(1) Markonikoff, *Ann.*, **302** (1899), 27.
(2) Markonikoff, *Ber.*, **30** (1897), 1223.
(3) Young, *J. Chem. Soc.*, **73** (1898), 906.
(4) Aschan, *Ber.*, **31** (1898), 1804.

neutral substance of camphor-like odour, m.p. 176–178°, and of unknown chemical nature, were isolated from the reaction product, and the two acids were confirmed by the characteristic odour and melting point determination (m. p. 183°) respectively.

The formation of methyl-cyclopentane from cyclohexanol, by the contact action of the acid earth at 330°, with decrease in the carbon ring $C_6$ to $C_5$, is completely analogous to the so-called rearrangement, the "retropinacoline rearrangement," suggested by Tiffeneau,[1] of alcohols of the cyclohexane series. Such conversion of the cyclohexane ring into the cyclopentane ring was carried out previously by Markonikoff[2] with amino cyclohexane and hydrogen iodide, and by Zelinski[3] with iodocyclohexane.

The assumption of an intermediate formation of cyclohexene, in the way, from cyclohexanol to methyl-cyclopentane, was examined experimentally by transforming the former compound isolated from the reaction product which was obtained by passing cyclohexanol on the earth at 200°, into methyl-cyclopentane.

From 40.8 gr. of the fraction (b.p. 82–84°) mentioned in Table 1, by passing on the earth heated at 330°, 29 gr. of oil ($d_{20}^{20}=0.7942$), 0.5 gr. of ethylene, and 1.2 gr. of water were obtained. The oily reaction product was fractionated into the following 6 portions, and each fraction was studied for density and index of refraction.

Table 5.

| Fraction | Yield gr. | $d_{20}^{20}$ | $n_D^{20}$ |
|---|---|---|---|
| 70–73° | 3.8 | 0.7464 | 1.41044 |
| 73–75° | 3.4 | 0.7533 | 1.41301 |
| 75–77° | 4.3 | 0.7567 | 1.41441 |
| 77–100° | 2.9 | 0.7613 | 1.41790 |
| 120–130° | 1.1 | 0.8123 | 1.45577 |
| Residue | 6.3 | 0.9387 | 1.54107 |

The fraction of b.p. 73–75° was confirmed to be mostly composed of methyl cyclopentane from the measurement of its physical constants. Higher boiling fractions were assumed, from their physical constants, to be composed of polymerized forms of cyclohexene.

When, however, 50 gr. of cyclohexane were treated under the same conditions as cyclohexene, no appreciable change took place, as will be shown in the results of fractionations of the product.

(1) Tiffeneau, *Ann.*, **405** (1914), 129.
(2) Markonikoff, *Ber.*, **31** (1898), 1223.
(3) Zelinski, *Ber.*, **30** (1899), 388.

TABLE 6.

| Fraction | Yield gr. | $d_{20}^{20}$ |
|---|---|---|
| 78-80°.7 | 32.7 | 0.7753 |
| 81-82° | 6.2 | 0.7780 |
| 82-85° | 8.9 | 0.7785 |

It is probable that hexamethylene, by the catalytic action of the Japanese acid earth, rearranges itself, at least in part, to form the more stable pentamethylene, even in case of these compounds in which one or more of the hydrogen atoms of the nucleus is replaced by a methyl group, or other long paraffine side-chains; and it is reasonable to suppose that these compounds would react in a manner analogous to that of the mother alcohol itself, since methyl cyclohexanone and menthone behave in a similar way as cyclohexanone toward lead peroxide and sulphuric acid.[1]

To demonstrate the above speculation, methyl cyclohexanol (1 : 2) prepared from o-cresol by catalytic reduction with reduced nickel and hydrogen at 180° (b.p. 167–170°; $d_{20}^{20}=0.9330$; $d_0^0=0.9473$; $n_D^{20}=1.45998$), was passed over the earth heated at 250° and 350° respectively, and the following results were obtained.

When 150 gr. of the alcohol treated at 250°, in presence of the catalyst, 94.0 gr. of oil, 21.3 gr. of water and some gaseous substance were obtained, and the former was divided into the following 11 portions after fractional distillation 10 times.

TABLE 7.

| No. | Fraction | Yield gr. | $d_0^0$ | $d_{20}^{20}$ | $d_0^{20}$ | $n_\alpha^{20}$ | $n_D^{20}$ | $n_\gamma^{20}$ | Methyl cyclohexene, % (by Br-value.) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | to 86° | 2.7 | 0.7948 | 0.7783 | 0.7771 | 1.42658 | 1.42940 | 1.44115 | — |
| 2 | 86-90° | 2.9 | 0.7998 | 0.7846 | 0.7835 | 1.42940 | 1.43211 | 1.44331 | — |
| 3 | 90-95° | 4.2 | 0.8018 | 0.7859 | 0.7847 | 1.43090 | 1.43362 | 1.44498 | 90.55 |
| 4 | 95-99° | 7.7 | 0.8039 | 0.7877 | 0.7866 | 1.43242 | 1.43512 | 1.44675 | 95.49 |
| 5 | 99-102° | 11.4 | 0.8047 | 0.7902 | 0.7891 | 1.43383 | 1.43652 | 1.44841 | 98.45 |
| 6 | 102-105° | 13.4 | 0.8082 | 0.7925 | 0.7913 | 1.43565 | 1.43843 | 1.45059 | 99.33 |
| 7 | 105-110° | 13.8 | 0.8135 | 0.7983 | 0.7974 | 1.43847 | 1.44125 | 1.45362 | about. 100 |
| 8 | 110-115° | 1.6 | 0.8228 | 0.8085 | 0.8074 | 1.44248 | 1.44451 | — | — |
| 9 | 115-120° | 1.4 | 0.8279 | 0.8133 | 0.8121 | 1.44300 | 1.44597 | — | — |
| 10 | 120-170° | 1.0 | 0.8645 | 0.8497 | 0.8485 | 1.44812 | 1.45092 | — | — |
| 11 | Residue | 16.2 | — | — | — | — | — | — | — |

(1) O. Wallach, Mathilde Gerhardt and W. Jessen, *J. Chem. Soc.*, 110 (1916), 487.

The fraction of b.p. 90–95° was confirmed as composed of methyl cyclohexenes by its physical constants, elementary analysis (C=86.58; H=13.32%) and also by the bromine-test, and other fractions with b.p. from 95–99° to 105–110° were also ascertained, in a similar manner to that of the third fraction, to consist of methyl cyclohexenes.

The occurrence of methyl-cyclohexene in the fractions mentioned above, was demonstrated by transforming the hydrocarbons present in the fractions with b.p. 99–102° and 102–105° with conc. nitric acid into an acidic sudstance with a m.p. of 152–153°, which shows no lowering of its melting point when mixed with pure adipic acid.

When 150 gr. of the methyl-cyclohexanol were passed over the catalyst heated at 350°, 118.4 gr. of oil ($d_0^{20}=0.8174$; $n_D^{20}=1.46145$) and 26.5 gr. water were obtained, and the oily substance was treated, to isolate some derivatives of cyclopentane formed from methyl-cyclohexanol by contact action of the catalyst, with conc. sulphuric acid to remove the unsaturated hydrocarbons formed from the alcohol, from the saturated ones which occur in the oil. The saturated hydrocarbons which remained, escaped from the reaction of the conc. sulphuric acid, were composed of 25 gr. of a liquid whose boiling point was 80–120°, and 12.4 gr. of another one of higher boiling point. The latter was divided into two fractions by steam distillation, namely 6.4 gr. of volatile ($d_0^{20}=0.8806$) and 3.6 gr. of non-volatile part.

25 gr. of the fraction with b.p. 80–120° were fractionated 10 times, and were divided into the following 8 fractions, each fraction was studied for its density and for the index of refraction and the results are shown in Table 8.

TABLE 8.

| No. | Fraction | Yield gr. | d | $d_{20}^{20}$ | $d_0^{20}$ | $n_\alpha^{20}$ | $n_D^{20}$ | $n_\gamma^{20}$ | Molecular dispersion |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 85–90° | 1.7 | 0.7656 | 0.7498 | 0.7488 | 1.41050 | 1.41212 | 1.42163 | — |
| 2 | 90–92° | 1.4 | 0.7716 | 0.7552 | 0.7541 | 1.41311 | 1.41515 | 1.42460 | 0.83 |
| 3 | 92–94° | 1.3 | 0.7747 | 0.7589 | 0.7578 | 1.41482 | 1.41680 | — | — |
| 4 | 94–96° | 2.4 | 0.7763 | 0.7612 | 0.7601 | 1.41592 | 1.41810 | 1.42763 | — |
| 5 | 96–98° | 5.2 | 0.7789 | 0.7634 | 0.7623 | 1.41723 | 1.41940 | 1.42884 | — |
| 6 | 98–101° | 7.7 | 0.7815 | 0.7665 | 0.7654 | 1.41853 | 1.42050 | 1.43008 | 0.78 |
| 7 | 101–104° | 1.9 | 0.7850 | 0.7694 | 0.7683 | 1.42034 | 1.42250 | — | — |
| 8 | Residue | 0.9 | — | — | — | — | — | — | — |

As will be seen in the above table, the fraction of b.p. 90–92° was noticed to be composed of dimethyl cyclopentane from its physical constants (index of refraction, density and dispersion), and this was also confirmed by elementary analysis: C=85.12; H=15.02, $C_7H_{14}$ requires C=85.71;

H=14.29%. Thus, the occurrence of dimethyl cyclopentane in the reaction product, due to the contact isomerisation of methyl cyclohexene, was demonstrated. The fraction with b.p. 98–101°, to our interest, was learned to be composed of methyl cyclohexane so far studied for its density, index of refraction and dispersion, and also for its elementary composition (C=85.53; H=14.62; $C_7H_{14}$ requires C=85.71; H=14.29%). For identification, it was subjected to contact oxidation by passing it on reduced nickel heated at 350° and toluene was obtained. This hydrocarbon was regarded as originating the contact action of conc. sulphuric acid on methyl cyclohexene, which was used in the previous treatment to clear the unsaturated hydrocarbons from the saturated ones, since methyl cyclohexene, according to Maquenne's report,[1] was actually transformed by the contact action of the acid into methyl cyclohexane.

In order to get more precise knowledge of the formation of methyl cyclohexane from methyl cyclohexene during the treatment, and also the occurrence of its isomeric dimethyl cyclopentane and methyl cyclohexenes in the reaction product, 150 gr. of the alcohol were treated with the earth heated at 350°, in a similar manner as the previous example. 112.4 gr. of oily product ($d_0^0$=0.8363) were obtained, which was then subjected to fractional distillation 10 times without treatment with sulphuric acid and the following 11 portions were obtained.

Table 9.

| No. | Fraction | Yield gr. | $d_0^0$ | $d_{20}^{20}$ | $d_5^{20}$ | $n_\alpha^{20}$ | $n_D^{20}$ | $n_\gamma^{20}$ | Methyl cyclohexene % (by Br-value) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 75–78° | 2.7 | 0.7659 | 0.7489 | 0.7481 | 1.41352 | 1.41610 | 1.42656 | — |
| 2 | 78–82° | 3.6 | 0.7792 | 0.7610 | 0.7602 | 1.41844 | 1.42095 | — | — |
| 3 | 82–89° | 4.3 | 0.7847 | 0.7677 | 0.7669 | 1.42135 | 1.42390 | 1.43489 | 22.10 |
| 4 | 89–92° | 5.2 | 0.7879 | 0.7720 | 0.7712 | 1.42401 | 1.42670 | 1.43734 | — |
| 5 | 92–95° | 7.2 | 0.7930 | 0.7760 | 0.7753 | 1.42668 | 1.42930 | — | — |
| 6 | 95–99° | 7.8 | 0.7961 | 0.7793 | 0.7784 | 1.42909 | 1.43191 | 1.44331 | 82.95 |
| 7 | 99–102° | 16.1 | 0.8067 | 0.7901 | 0.7893 | 1.43585 | 1.43863 | — | 98.25 |
| 8 | 102–105° | 14.6 | 0.8134 | 0.7976 | 0.7967 | 1.44109 | 1.44416 | 1.45716 | 99.87 |
| 9 | 105–110° | 16.5 | 0.8224 | 0.8060 | 0.8051 | 1.44671 | 1.44987 | 1.46366 | about 100 |
| 10 | 110–120° | 2.0 | 0.8361 | 0.8191 | 0.8182 | 1.45463 | 1.45807 | 1.47274 | — |
| 11 | Residue | 21.6 | — | — | — | — | — | — | — |

The reaction product, from its physical constants, elementary analysis and also the bromine value measured following the directions of

(1) Maquenne, *Bull. Soc. Chim.*, [3] 9 (1893), 129.

McIlhiney,[1] was considered to be composed of 20% dimethyl cyclopentane and 40% methyl cyclohexene. The fraction with b.p. 99–102°, after being confirmed to be composed of methyl cyclohexene but not cyclohexane, was subjected to oxidation with conc. nitric acid, and oxalic, succinic, adipic (this being the main product) and β-methyl adipic acids were isolated from the reaction product, and also were ascertained by the determination of the melting point.

From the above investigations, it is evident that methyl cyclohexanol, when heated at 250° in presence of the Japanese acid earth, yields methyl cyclohexene as main reaction product, while at 350° the reaction proceeded to form dimethyl cyclopentane from some part of the methyl cyclohexene, but the isomerisation of hexamethylene to pentamethylene hydrocarbon takes place usually under high pressure. Further course of the reaction involved is not clear, but the products are olefines of low molecular weight and polymers of the unsaturated hydrocarbons.

Thus, the contact isomerisation of hydrocarbons of the polymethylene series, besides promoting the actions of dehydration and polymerisation, was forced to denote a special feature of the contact actions of the Japanese acid earth.

Tokyo Imperial Industrial Laboratory,
Hatagaya, Tokyo.

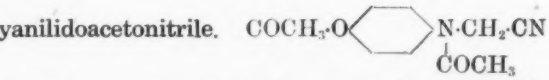
---

## SOME DERIVATIVES OF HYDROXYPHENYLGLYCINE. II.

By **Kotaro SHIMO.**

Received July 29, 1926. **Published October 28, 1926.**

***Acetyl or Benzoyl Derivatives of Hydroxyphenylglycine Nitriles.***

**1. Diacetyl-p-hydroxyanilidoacetonitrile.** 

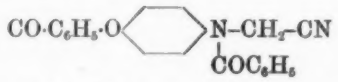
7.4 Gr. of the nitrile were treated with 11.5 c.c. of acetic anhydride, in an alkaline solution, 8 gr. of diacetyl-p-hydroxyanilidoacetonitrile was obtained, which was recrystallised several times from 50% alcohol, in small white platy crystals melting at 94–95° (uncorr.). Galatis[2] described 75° for its

(1) McIlhiney, *J. Soc. Chem. Ind.*, **13** (1894), 668.
(2) See this journal **1** (1926), 202.

melting point. The analytical results and chemical properties of this substance agree with those described by Galatis.

0.1763 gr. subst. gave 0.4028 gr. $CO_2$ and 0.0807 gr. $H_2O$. 0.1888 gr. subst. gave 18.8 c.c. $N_2$ (9°, 765 mm.). (Found: C=62.31; H=5.09; N=12.47. $C_{12}H_{12}O_3N_2$ requires C=62.07; H=5.17; N=12.07%).

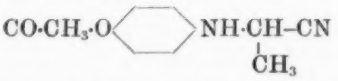
2. **Dibenzoyl-p-hydroxyanilido-acetonitrile.**



It was prepared by the action of benzoyl chloride on p-hydroxyanilido-acetonitrile in alkaline solution, and found to melt at 129–130° (uncorr.).

0.1092 gr. subst. gave 0.2980 gr. $CO_2$ and 0.0462 gr. $H_2O$. 0.0921 gr. subst. gave 6.3 c.c. $N_2$ (10.5°, 749.4 mm.). (Found: C=74.40; H=4.70; N=8.16. $C_{11}H_{12}O_3N_2$ requires C=74.16; H=4.49; N=7.87%).

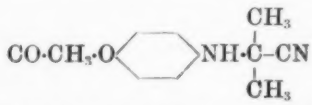
3. **Acetyl-p-hydroxyanilidomethyl-acetonitrile.**



The acetyl compound was obtained by acetylation of the nitrile by means of acetic anhydride and sodium acetate at room temperature. The pure substance was obtained as small platy crystals melting at 129–131° (uncorr.).

0.1136 gr. subst. gave 0.2683 gr. $CO_2$ and 0.0617 gr. $H_2O$. 0.1031 gr. subst. gave 12.2 c.c. $N_2$ (13°, 757.5 mm.). (Found: C=64.41; H=6.31; N=14.14. $C_{11}H_{12}O_2N_2$ requires C=64.71; H=5.88; N=13.73%).

4. **Acetyl-p-hydroxyanilidodimethyl-acetonitrile.**



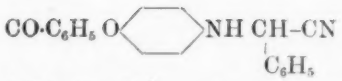
The nitrile was acetylated with acetic anhydride in alkaline solution and the crude product was purified from alcohol solution. The pure substance is beautiful long needles and melts at 77–78° (uncorr.).

0.1195 gr. subst. gave 0.2875 gr. $CO_2$ and 0.0712 gr. $H_2O$. 0.1059 gr. subst. gave 11.3 c.c. $N_2$ (9.5°, 764 mm.). (Found: C=65.61; H=6.67; N=13.02. $C_{12}H_{14}O_2N_2$ requires C=66.05; H=6.42; N=12.85%.)

The nitrile, however, on benzoylation by means of Schotten-Bauman's method instead of the expected benzoyl derivative, dibenzoyl-p-aminophenol, melting at 233–234° (uncorr.) was the result.

0.1121 gr. subst. gave 4.25 c.c. $N_2$ (11.5°, 761.5 mm.). (Found: N=4.58. $C_{20}H_{15}O_3N$ requires N=4.42%).

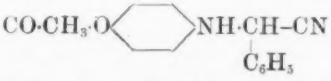
**5. Benzoyl-p-hydroxyanilidophenyl-acetonitrile.**



The nitrile was benzoylated by means of Schotten-Bauman's method and the benzoyl derivative which was recrystallised from alcohol, began to sinter at 160° and melted clear at about 200°.

0.1209 gr. subst. gave 0.3389 gr. $CO_2$ and 0.0537 gr. $H_2O$. 0.1336 gr. subst. gave 8.1 c.c. $N_2$ (13.5°, 762.6 mm.). (Found : C=76.63 ; H=4.97 ; N=8.95. $C_{21}H_{16}O_2N_2$ requires C=76.83 ; H=4.89 ; N=8.54%).

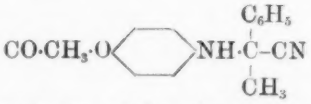
**6. Acetyl-p-hydroxyanilidophenyl-acetonitrile.**



The nitrile was acetylated by means of acetic anhydride, in alkaline solution, and the pure acetyl derivative melting at 119–120° was obtained as small hexagonal crystals.

0.1262 gr. subst. gave 0.3330 gr. $CO_2$ and 0.0601 gr. $H_2O$. 0.1067 gr. subst. gave 9.8 c.c. $N_2$ (9°, 758 mm.). (Found : C=71.97 ; H=5.29 ; N=11.14. $C_{16}H_{14}O_2N_2$ requires C=72.18 ; H=5.26 ; N=10.53%).

**7. Acetyl-p-hydroxyanilidophenylmethyl-acetonitrile.**



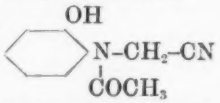
The acetyl compound was obtained by acetylation of the nitrile either by acetic anhydride in alkaline solution or by acetic anhydride and sodium acetate. It was purified by dilute alcohol and the pure substance melts at 142–143° (uncorr.).

0.1137 gr. subst. gave 0.3042 gr. $CO_2$ and 0.0587 gr. $H_2O$. 0.1059 gr. subst. gave 9.0 c.c. $N_2$ (8°, 759.4 mm.). (Found : C=72.97 ; H=5.78 ; N=10.36. $C_{17}H_{16}O_2N_2$ requires C=72.86 ; H=5.71 ; N=10.00%).

By the action of benzoyl chloride and alkali on the nitrile, dibenzoyl-p-aminophenol melting at 233–234° (uncorr.) was obtained.

0.1025 gr. subst. gave 0.2851 gr. $CO_2$ and 0.0452 gr. $H_2O$. (Found : C=75,86 ; H=4.90. $C_{20}H_{15}O_3N$ requires C=75.71 ; H=4.73%).

**8. Acetyl-o-hydroxyanilidoacetonitrile.**



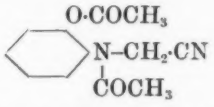
When the crude nitrile which was extracted with ether from the reaction mixture, above mentioned,[1] was acetylated immediately by acetic anhydride, in alkaline solution, monoacetyl derivative was obtained. The pure sub-

(1) This journal 1 (1926), 206.

stance which was purified from alcohol solution is fine colorless cubic crystals melting at 167–168° (uncorr.). It shows a pale reddish violet coloration with ferric chloride, yellowish red coloration with conc. nitric acid and red coloration with Millon's reagent.

0.1249 gr. subst. gave 0.2893 gr. $CO_2$ and 0.0606 gr. $H_2O$. 0.1064 gr. subst. gave 13.25 c.c. $N_2$ (10°, 757 mm.). (Found: C=63.17; H=5.39; N=15.03. $C_{10}H_{10}N_2O_2$ requires C=63.30; H=5.26; N=14.74%).

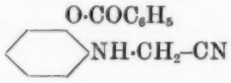
9. **Diacetyl-o-hydroxyanilidoacetonitrile.**



When the pure nitrile was acetylated with acetic anhydride and sodium acetate at room temperature, the diacetyl cempound was obtained. It consists of colorless needles which melt at 105–106° (uncorr.).

0.1203 gr. subst. gave 0.2715 gr. $CO_2$ and 0.0603 gr. $H_2O$. 0.1055 gr. subst. gave 10.8 c.c. $N_2$ (9.5°, 753.4 mm.). (Found; C=61.55; H=5.57; N=12.37. $C_{12}H_{12}O_3N_2$ raquires C=62.07; H=5.17; N=12.07%).

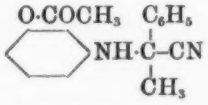
10. **Benzoyl-o-hydroxyanilidoacetonitrile.**



The nitrile was benzoylated by Schotten-Bauman's method. The benzoyl-o-hydroxyanilidoacetonitrile was obtained as fine white crystalline powder melting at 120–121° (uncorr.).

0.1121 gr. subst. gave 0.2942 gr. $CO_2$ and 0.0504 gr. $H_2O$. 0.1337 gr. subst. gave 12.7 c.c. $N_2$ (13°, 755.8 mm.). (Found: C=71.56; H=5.00; N=11.33. $C_{15}H_{12}O_2N_2$ requires C=71.43; H=4.76; N=11.11%).

11. **Acetyl-m-hydroxyanilidophenylmethyl-acetonitrile.**

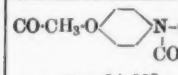
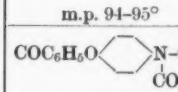
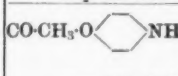
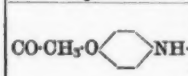
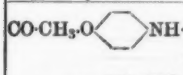
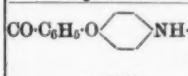
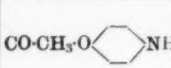
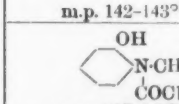
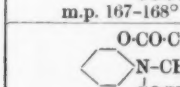
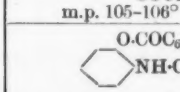
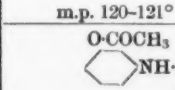


When the nitrile was acetylated by acetic anhydride and sodium acetate, the acetyl compound was obtained which was purified by dilute alcohol. It melts at 123–124° (uncorr.).

0.1199 gr. subst. gave 0.3182 gr. $CO_2$ and 0.0630 gr. $H_2O$. 0.1059 gr. subst. gave 8.9 c.c. $N_2$ (11°, 766.5 mm.). (Found: C=72.38; H=5.88; N=10.42. $C_{17}H_{16}O_2N_2$ requires C=72.86; H=5.71; N=10.00%).

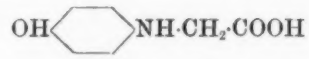
The solubilities of the acetyl or benzoyl derivatives of hydroxyphenylglycinenitriles in organic solvents and also in acids or alkalies are mentioned in Table 1.

TABLE 1.

| Substance. | Acetone, alcohol, acetic ester, or glac. acetic acid. | Benzene, ether or chloroform. | Ligroin or water. | Caustic alkalies or mineral acids. |
|---|---|---|---|---|
|  m.p. 94–95° | soluble. | soluble. spar. sol. in ether. | sol. in hot water. | insoluble. |
|  m.p. 129–130° | soluble. | soluble. | insoluble. | insoluble. |
|  m.p. 129–131° | soluble. | soluble. | spar. soluble. | sol. in acid. insol. in alkali. |
|  m.p. 77–78° | soluble. | soluble. | insoluble. | sol. in acid. insol. in alkali. |
|  m.p. 119–120° | soluble. | soluble. | insoluble. | insoluble. |
|  m.p. 200° | soluble. | soluble. spar. sol. in ether. | insoluble. | insoluble. |
|  m.p. 142–143° | soluble. | soluble. | insoluble. | insoluble. |
|  m.p. 167–168° | soluble. | spar. sol. | spar. sol. in water. | soluble in alkali. insol. in acid. |
|  m.p. 105–106° | soluble. | soluble. | spar. sol. | insoluble. |
|  m.p. 120–121° | soluble. | spar. sol. sol. in chloroform. | insol. in water. | sol.in conc. HCl. insol. in alkali. |
|  m.p. 123–124° | soluble. | soluble. | insoluble. | insoluble. |

*Derivatives of Hydrophenylglycine.*

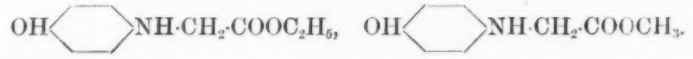
**1. p-Hydroxyanilidoacetic Acid.**
**(p-Hydroxyphenylglycine.)**



This substance was obtained from p-hydroxyanilidoacetonitrile by saponifying with dilute caustic soda in 84.2% yield of the theory.

0.1822 gr. subst. gave 0.3823 gr. $CO_2$ and 0.0885 gr. $H_2O$. 0.1537 gr. subst. gave 10.7 c.c. $N_2$ (10°, 764 mm.). (Found : C=57.28 ; H=5.40 ; N=8.48. $C_8H_9O_3N$ requires C=57.49 ; H=5.39 ; N=8.38%).

**2. Ethyl and Methyl Ester of p-Hydroxyanilidoacetic Acid.**

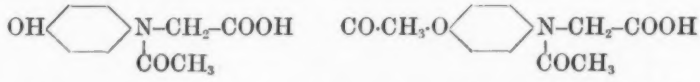


p-Hydroxyanilidoacetic acid yield the ethyl and methyl ester when dry hydrogen chloride gas was passed into the corresponding alcoholic solution of the acid, and then neutralising hydrochloride of the ester with sodium carbonate solution. The ethyl ester, thus obtained, was white leaflets, melting at 78–79° (uncorr.) and methyl ester at 97–98° (uncorr.).

0.1663 gr. of the ethyl ester gave 0.3748 gr. $CO_2$ and 0.0989 gr. $H_2O$. 0.1932 gr. of the subst. gave 12.25 c.c. $N_2$ (19°, 751.4 mm.). (Found : C=61.47 ; H=6.61 ; N=7.36. $C_{10}H_{13}O_3N$ requires C=61.54 ; H=6.67 : N=7.18%).

0.1695 gr. of the methyl ester gave 0.3696 gr. $CO_2$ and 0.0910 gr. $H_2O$. 0.1562 gr. of the subst. gave 10.6 c.c. $N_2$ (20°, 753 mm.). (Found : C=59.47 ; H=5.97 ; N=7.87. $C_9H_{11}O_3N$ requires C=59.67 ; H=6.08 ; N=7.74%).

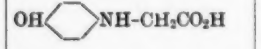
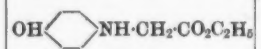
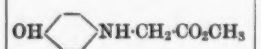
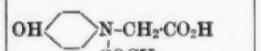
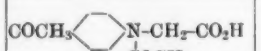
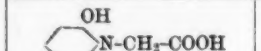
**3. Mono-and Di-acetyl-p-hydroxyanilidoacetic Acid.**



When p-hydroxyanilidoacetic acid is treated with acetic anhydride in alkaline solution, it yields diacetyl-p-hydroxyanilidoacetic acid which melts at 174–175° (uncorr.). When, however, ethereal solution of acetic anhydride is used as an acetylation agent monoacetyl derivative is formed, which crystallizes from hot aqueous solution in white prisms, melting at 203–204° (uncorr.).

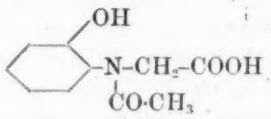
0.1566 gr. of the diacetyl subst. gave 0.3263 gr. $CO_2$ and 0.0736 gr. $H_2O$. 0.1728 gr. of the subst. gave 8.6 c.c. $N_2$ (18°, 753.5 mm.). (Found : C=56.81; H=5.22 ; N=5.82. $C_{12}H_{13}O_5N$ requires C=57.37 ; H=5.18 ; N=5.58%).

TABLE 2.

| Substance. | Solubility. | | | Color Reaction. | | |
|---|---|---|---|---|---|---|
| | Acetone, alcohol, ether, chloroform, acetic ester, benzene, or glac. acetic acid. | Water. | Caustic alkalies or mineral acids. | Ferric chloride. | Silver nitrate. | Am. silver nitrate. |
|  | sparingly soluble. | spar. sol. | soluble. | violet-red. | greyish black ppt. | pale brownish yellow → blue colloidal. |
|  m.p. 78–79°  m.p. 97–98° | soluble. | sol. in hot. spar. sol. in cold. | soluble. | reddish violet. | pale reddish violet producing white ppt. | yellowish green colloidal → dirty green → greyish black ppt. |
|  m.p. 203–204° | sparingly soluble. sol. in alcohol or acetone. | sol. in hot. spar. sol. in cold. | soluble in alkali. | pale dirty violet. | | |
|  m.p. 174–175° | soluble. spar. sol. in ether or benzene. | sol. in hot. spar. sol. in cold. | soluble in alkali. | | | |
|  m.p. 201–202° | soluble. spar. sol. in ether, chloroform or benzene. | spar. sol. | soluble in alkali. insoluble in acid. | pale reddish violet. | | |

0.1844 gr. of the monoacetyl subst. gave 0.3868 gr. $CO_2$ and 0.0857 gr. $H_2O$. 0.1721 gr. of the subst. gave 10.1 c.c. $N_2$ (18.5°, 753.9 mm.). (Found ; C=57.21; H=5.16 : N=6.85. $C_{10}H_{11}O_4N$ requires C=57.41 ; H=5.26 ; N=6.70%).

**4. Acetyl-o-hydroxyanilidoacetic Acid (Acetyl-o-hydroxyphenylglycine).**




Acetyl-o-hydroxyanilidoacetonitrile was boiled with dilute caustic soda until the evolution of ammonia had ceased, and then the solution was acidified with hydrochloric acid, whereby slightly brown-coloured sandy crystals were deposited.

Acetyl-o-hydroxyphenylglycine recrystallised from boiling water is colourless monoclinic crystals and melt at 201–202° (uncorr.) with slight decomposition.

0.1112 gr. subst. gave 0.2324 gr. $CO_2$ and 0.0537 gr. $H_2O$. 0.1267 gr. subst. gave 7.5 c.c. $N_2$ (13°, 755.5 mm.). (Found : C=57.00 ; H=5.40; N=7.08. $C_{10}H_{11}O_4N$ requires C=57.41 ; H=5.36 ; N=6.70%).

The solubility and the colour reactions of the derivatives of hydroxyphenylglycine are mentioned in Table 2.

The Imperial Industrial Research Institute of Osaka,
Daini, Osaka.

---

# ÉTUDES DE DÉRIVÉS DU FURFURAL.
## III. SUR LA TEINTE EN PASSAGE DES CÉTONES FURYLIQUES.

Par **Itizo KASIWAGI.**

Reçu le 21 août 1926. Publié le 28 octobre 1926.

On a déjà observé que les solutions des cétones furyliques se colorent sous l'action des alcalis caustiques du rouge clair au rouge brunâtre.[1] Ce sont les cétones furyliques avec les chaînes latérales *saturées* comme

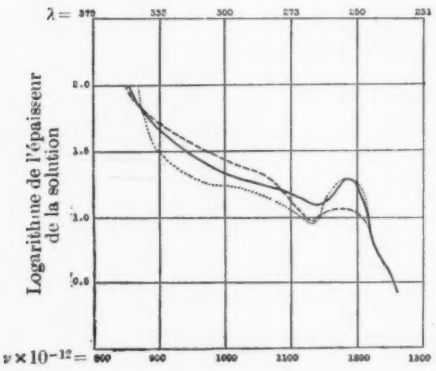
| | |
|---|---|
| furylbutanone | $C_4H_3O{\cdot}CH_2\,CH_2\,CO{\cdot}CH_3$, |
| furylpentanone | $C_4H_3O\,CH_2\,CH_2\,CO{\cdot}CH_2{\cdot}CH_3$, |
| difuryloctadione | $\begin{matrix} C_4H_3O\,CH\,CH_2\,CO\,CH_3 \\ \vert \\ C_4H_3O\,CH\,CH_2\,CO\,CH_3 \end{matrix}$, |

(1) I. Kasiwagi, ce journal, **1** (1926), 145.

furfurylcamphre $C_4H_3O{\cdot}CH_2{\cdot}CH(C_8H_{14})—CO$, etc.,

qui présentent ce phénomène.

Pour étudier cette coloration, nous avons pris tout d'abord les photographies de spectres d'absorptions. Dans ce but on a distillé les cétones mentionnées, on a préparé les solutions alcooliques à 1/100 N ajoutées avec l'éthylate de sodium en quantité équivalente, et il en a été résulté des solutions tout à fait incolores. Nous avons pensé que les solutions étaient trop étendues. Puis, en comparant les courbes de spectres d'absorptions des cétones seules avec celles des cétones en présence de l'alcali, on a trouvé qui les unes et les autres sont presque identiques (Fig. 1 et 2), c'est-à-dire que les cétones semblent ne subir aucune réaction en présence de l'alcali.

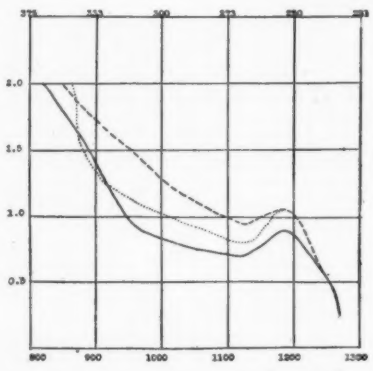



—— Furylbutanone antérieurement distillée; solution alcoolique à 1/100 N en présence de l'éthylate de sodium en quantité équivalente.

- - - - Furylbutanone à la même condition, mais fraîchement distillée.

····· Furylbutanone seule, en solution alcoolique à 1/100 N.

Fig. 1.



—— Furylpentanone antérieurement distillée; solution alcoolique à 1/100 N en présence de l'éthylate de sodium en quantité équivalente.

- - - - Furylpentanone à la même condition, mais fraîchement distillée.

····· Furylpentanone seule, en solution alcoolique à 1/100 N.

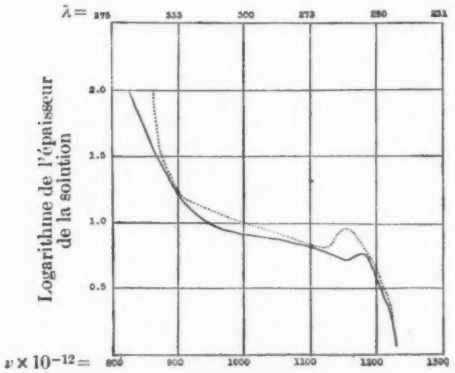
Fig. 2.

Lorsque nous avons préparé le furylcamphre, nous avons éssayé si ce corps donne la même coloration avec l'alcali, et nous avons trouvé qu'il ne la donne pas *au moins* aux yeux. Les autres produits des cétones en solutions alcooliques se colorent en rouge en présence de l'alcali, comme les alcalis

caustiques, les carbonates d'alcalis, l'ammoniaque, l'éthylate de sodium, etc. Les solutions rouges passent à leur tour au jaune après quelques heures.

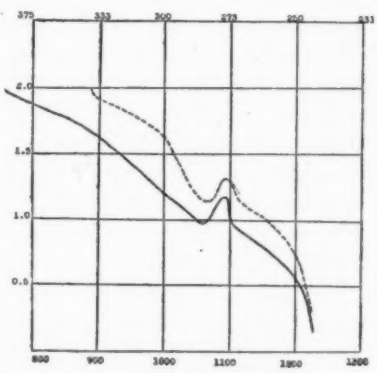
Les résultats expérimentaux nous ont permis de tirer la conclusion que la coloration est attribuable à l'existence de composés inconnus formés soit par condensation soit par polymérisation des cétones, ayant absorbé les rayons ultraviolets, car il semble que cette formation des composés marche avec une certaine vitesse, et les cètones étudiées possèdent sans exception les bands d'absorptions dans cette région.[1]

La tendance de se polymériser ou s'assodier du furfural et de ses dérivés a fait l'objet de nombreuses études. Getman a étudié l'association du furfural par voie cryoscopique, et il a constaté l'existence des molécules plus ou moins associées.[2] Toutes ces activités chimiques sont, de l'avis de ce savant américain,[3] dues à l'absorption des rayons dans la région ultraviolette, et naturellement le noyau furanique joue le rôle principal.




—— Furfurylcamphre; solution alcoolique à 1/100 N en présence de l'éthylate de sodium en quantité équivalente.
····· Furfurylcamphre seul en solution alcoolique à 1/100 N.

Fig. 3.



—— Difuryloctadione ; solution alcoolique à 1/100 N en présence de l'éthylate de sodium.
- - - - Difuryloctadione seule; en solution alcoolique à 1/100 N.

Fig. 4.

## Partie expérimentale.

*Ier éssai :* Les solutions alcooliques des cétones citées ci-dessus donnent sans exception la coloration rouge avec l'alcali, au bout d'un certain temps, un jour environ, après la purification, soit par distillation soit par cristallisation.

(1) I. Kasiwagi, ibid., **1** (1926), 147.
(2) Getman, *J. Phys. Chem.*, **29** (1925), 395.
(3) Getman, ibid., **28** (1924), 397.

Au contraire les solutions ne donnent pas la coloration, quand on dissout les cétones tout de suite après la purification.

*2ème éssai :* Les cétones, ainsi que les résidus de distillation de ces corps, se colorent en solutions alcooliques avec les alcalis. Les salutions rougies passent au jaune clair après une dizaine d'heures.

*3ème éssai :* Les solutions alcooliques sans couleur se teignent en brun ou rouge brunâtre après plusieurs heures, tandis que les solutions aqueuses ou suspensions dans l'eau (également incolores quand les cétones sont fraîchement distillées) ne se colorent pas. Seulement après une demidouzaine de jours celles-ci colorent faiblement en jaune, bien que la solubilité soit apparemment beaucoup moindre en eau qu'en alcool.

*4ème éssai :* Les solutions rouges passent au jaune claire, quand on les chauffe. Les solutions rougies par l'ammoniaque jaunissent pareillement par l'addition de l'acide, et elles ne rougissent jamais, étant rendues alcalines par l'ammoniaque et, au contraire, elles passent au jaune plus foncé. Ces réactions—les changements de couleurs—semblent irréversibles.

*5ème éssai : Études spectrographiques.* Sur le dispositif spectrographique voir le deuxième mémoire.[1]

On voit plus ou moins la proportionnalité des déplacements des courbes d'absorptions avec la durée de la distillation des corps étudies jusqu'à la dissolution. Les courbes d'absorptions de la difuryloctadione en sont un bon exemple, car elles sont presque identiques sauf que l'une de la solution en prèsense de l'alcali indique l'absorption plus profonde vers le spectre visible. Cette dione que nous nous sommes servie fond à 119.5–120°.

Ces observations spectrographiques coincident très bien avec les éssais cités, et tous ces résultats expérimentaux nous permettent de conclure la formation des composés intermédiaires qui donnent cette coloration caractéristique avec l'alcali, et aussi que ces composés sont assez labiles.

Haute école polytechnique de Yokohama.

(1) I. Kasiwagi, loc. cit.